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Bi-Ionic Potentials across Liquid Anion Exchanger Membranes

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Summary. The bi-ionic potentials, B.I.P.'s, arising in cells of the type: $A^+L^-c_1$ | liquid anion exchanger membrane of extreme anionic selectivity | $A^+M^-c_1$, are surveyed briefly but systematically. The membranes consisted of trioctyl-propyl ammonium salts dissolved in *o*-dichlorobenzene. As anticipated on the basis of previous theoretical and experimental work on porous membranes, the following regularities were observed. The B.I.P. arising with any pair of critical ions is essentially independent of the activity of the aqueous electrolytic solutions used, and is essentially independent of the degree of loading of the membrane with ion-exchanger compound. The B.I.P.'s are higher the farther apart the two critical anions under consideration, L^- and M^-, are in the Hofmeister series, −443 mV in the case of the $\mathrm{B.I.P.}_{\mathrm{ClO}_4^-/\mathrm{IO}_3^-}$ the iodate solution being negative. The B.I.P.'s, as shown in a series of 21 cells with seven different univalent critical ions are algebraically additive, in the sense that within the limits of the experimental error

$$\mathrm{B.I.P.}_{L^-/M^-} + \mathrm{B.I.P.}_{M^-/N^-} = \mathrm{B.I.P.}_{L^-/N^-},$$

where L^-, M^-, and N^- represent any arbitrary combination of the anions used.

The bi-ionic potential B.I.P. has been defined [8] as the dynamic membrane potential which arises across membranes of extreme (anionic or cationic) selectivity when interposed between solutions of the same concentration (more correctly of the same activity) of two electrolytes having different permeable, "critical", ions which are able to exchange across the same membrane, and (preferably) with the same species of "noncritical" counter ions for which the membrane is impermeable or virtually so [3]. Such cells in which the anions represent the critical ions are represented by the scheme:

$$\begin{array}{c|c|c} \text{Solution 1} & \text{Exclusively} & \text{Solution 2} \\ A^+L^-c_1 & \text{anion permeable} & A^+M^-c_1. \\ & \text{membrane} & \end{array}$$

The B.I.P. is the algebraic sum of the equilibrium potentials arising at the two solution-membrane interfaces and a liquid junction potential arising within the membrane. The more readily permeable species of critical ions impresses its charge on the other solution.

A simple theory of the B.I.P. arising across porous ion exchanger membranes was developed by Sollner [8] who also reviewed earlier experimental data and pertinent theoretical considerations. Sollner's ideas were elaborated on and refined by various other investigators; systematic experimental B.I.P. data were presented by Dray and Sollner [3] and others. The literature, including earlier reviews, has been reviewed briefly by Hale and Govindan [6].

In recent years, liquid ion exchanger membranes of highest ionic selectivity have been described [1, 10] and it appeared that with these membranes, too, B.I.P.'s of considerable magnitude could be anticipated and that essentially the same theoretical reasoning could be applied as in the case of the porous ion exchange membranes [10].

The liquid ion exchanger membranes consist of solutions of medium molecular weight ionogenic compounds, referred to here as RX, such as dinonyl naphthalene sulfonates or trioctyl-propyl-ammonium salts dissolved in water-insoluble solvents, such as *o*-dichlorobenzene or *o*-nitrotoluene. Such membranes when in contact with electrolytic solutions, readily exchange their inorganic counter ions.

Several investigations on B.I.P.'s across liquid ion exchanger membranes have been published; a recent one by Danesi, Salvemini, Scibona, and Scuppa [2] contains a review of this literature. However, the lack of a rigorous systematic approach mars the value of the available experimental data.

This paper presents systematic data to test several regularities predicted by the theory of the B.I.P. [2, 4, 6, 8] which have been demonstrated experimentally in the case of porous permselective membranes [3, 4]. *A priori*, one can expect to find the following regularities also with liquid ion exchanger membranes consisting of a given ion exchanger compound in a given solvent:

1) The B.I.P. should be essentially independent of the concentration (more correctly, activity) of the aqueous electrolytic solutions.

2) The B.I.P. arising with any pair of critical ions should be sensibly independent of the degree of loading of the membrane with ion exchanger compound.

3) The B.I.P. should be higher the farther apart the two critical ions under consideration are in the Hofmeister series (except in cells in which

one or the other of the species of critical ions interacts specifically with the solvent or exchanger, possibilities that are outside the scope of this paper).

4) The B.I.P.'s obtained with any set of univalent anions of strong electrolytes in solution, L^-, M^-, and N^-, should be algebraically additive in the sense that

$$\text{B.I.P.}_{L^-/M^-} + \text{B.I.P.}_{M^-/N^-} = \text{B.I.P.}_{L^-/N^-} \quad \text{(ref. [4]).} \qquad (1)$$

Experimental and Results

The general experimental prerequisites for meaningful B.I.P. measurements were outlined some time ago [3]; additional ones which apply specifically to liquid ion exchanger membranes were recently discussed elsewhere [9]. As pointed out there, to have the best defined experimental systems, it is necessary not only to employ membranes of extreme ionic selectivity and minimal water permeability [7, 11], but also to work with strong acid or strong base ion exchanger compounds whose various salt forms RX have very high membrane solvent/water distribution coefficients. The membrane solvent should have a dielectric constant that is not too low so that membranes of low ion exchanger content do not have excessively high resistances. Further factors which are helpful in creating the simplest, most nearly ideal experimental systems are: low concentrations of ion exchanger in the membrane; adequately high concentrations of the electrolyte solutions; and the use of electrolytes with critical ions high in the Hofmeister series. Last but not least, equilibrium conditions should prevail at the two solution-membrane phase boundaries. This condition is readily obtained if the two phases which form the phase boundary are equilibrated with each other before a cell is assembled.

Cells based on trioctyl-propyl ammonium salts (TOPA)X dissolved in *o*-dichlorobenzene (dielectric constant 9.9) can be readily assembled to fulfill the outlined requirements to a high degree. Cells consisting of these substances were used exclusively in the work described below. Rate of exchange studies, of the type reported previously [7, 11] with such membranes, showed ionic selectivities for anions over cations of $10^4:1$ to $10^5:1$ and better.

Fig. 1 shows a schematic drawing of our B.I.P. cells as used with membranes of specific gravity higher than the aqueous solutions, KI and KBr in the figure. The two outermost tubes of the cell which contain only aqueous solutions serve to prevent contamination of the solution-membrane interfaces with KCl when KCl bridges are inserted for potential measurements.

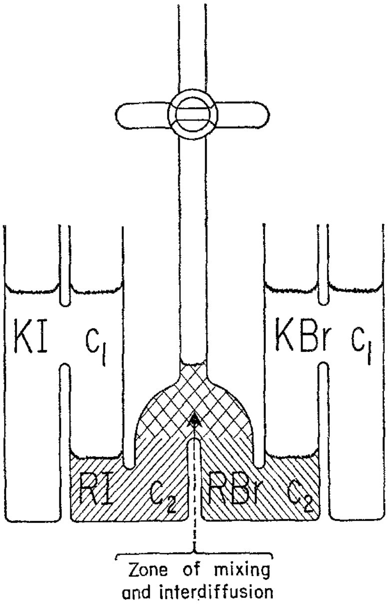

Fig. 1. Schematic drawing of B.I.P. cells as used with membranes of specific gravity higher than the aqueous solutions, KI and KBr

The aqueous KI solution in Fig. 1 was previously equilibrated with the RI part of the membrane, and the aqueous KBr solution with the RBr part of the membrane. The cells are designed so that mechanical mixing and interdiffusion of RI and RBr are restricted for a considerable time to the middle zone of the membrane. Thus, the phase boundaries remain in an undegraded, equilibrium state during the potential measurements.

All measurements were made at 25.00±0.05 °C immediately after the cells were assembled from the four thermally preequilibrated constituent solutions, using saturated KCl-agar bridges, saturated calomel electrodes and an electrometer connected to a digital voltmeter. All potentials given below are the raw experimental data; they are not corrected for the asymmetry of the two liquid junction potentials at the bridge-solution junctions. These corrections would be small and, moreover, without any significance in the demonstration of the regularities shown below.

To test the influence of the activity of the electrolyte solutions on the B.I.P., cells were studied in which the activities of the KI and KBr solutions were varied in the sequence 1.0, 0.1, 0.01, and 0.001. These solutions had been equilibrated with 0.02 M TOPA in the iodide form, (TOPA)I, or in the bromide form, (TOPA)Br, dissolved in *o*-dichlorobenzene. The corresponding B.I.P.'s were 139, 137, 137, and 133 mV, respectively, the KBr solutions being negative. This moderate decrease in the measured B.I.P. with decreasing solution concentration can be anticipated on theoretical grounds. The quantities of (TOPA)I and of (TOPA)Br dissolved in the two 0.1 M aqueous solutions are not equal; the compound with the critical ion lower in the Hofmeister series, (TOPA)Br, being more soluble. Though these solubilities are small, they are not negligible and increase with decreasing electrolyte activity in the aqueous solutions according to the mass action law [9]. Thus, the theoretical 1:1 activity ratio of the critical ions in these solutions is not strictly maintained and the measured EMF's become lower at the lower solution concentrations. These cells are not true "ideal" B.I.P. cells, but "two-ionic" cells as defined by Dray and Sollner [4]. This view is proven by the fact that in similar experiments in which the concentrations of the critical ions in the two aqueous solutions were determined analytically, the observed deviations could be calculated with a high degree of accuracy from the equations given by these investigators [4]. Thus, we must conclude that the highest of the potentials found in the above experiments is very close to the true, "ideal" B.I.P. of our cell [9].

To test the influence of the ion exchanger content of the membrane on the B.I.P., 0.1 M solutions of KI and KBr were equilibrated with solutions of 0.0002, 0.002, 0.02, and 0.2 M trioctyl-propyl ammonium ion exchanger in the iodide or bromide forms, (TOPA)I or (TOPA)Br, dissolved in *o*-dichlorobenzene. The B.I.P.'s obtained with these four cells were 140, 138, 137, and 134 mV, respectively, the KBr solutions being negative.

While nearly constant over a thousandfold range of membrane loading, the decrease in the EMF of these cells with increasing loading is significant from the experimental point of view and is based on the same physical effect as in the preceding case; namely, the differences in the solubilities of (TOPA)I and (TOPA)Br in the aqueous solutions which increase with increasing loading of the membrane with ion exchanger compound [9][1]. The "true" B.I.P. is very close to the value found with the lowest loading.

Table 1 contains a set of systematic B.I.P. data which pertains to 3) and 4) of the before-enumerated points, the importance of the Hofmeister anion series in B.I.P. cells, and the validity of the additivity rule as expressed in Eq. (1).

Seven electrolytes were paired against each other in all 21 possible combinations in cells of the type: 0.1 M aqueous electrolyte AL equilibrated with 0.02 M (TOPA)L in *o*-dichlorobenzene | 0.02 M (TOPA)L in *o*-dichloro-

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[1] Another probable complication, disregarded here, is that because of the equilibration as carried out in our experiments, the concentration of the ion exchanger in the two halves of the membrane (and therefore at the phase boundaries) may not be strictly the same.

benzene equilibrated with 0.1 M aqueous electrolyte AL | 0.02 M (TOPA) M in *o*-dichlorobenzene equilibrated with 0.1 M aqueous electrolyte AM | 0.1 M aqueous electrolyte AM equilibrated with 0.02 M (TOPA) M in *o*-dichlorobenzene. The accuracy and reproducibility of these measurements were, in most instances, better than 0.5 mV. The sign of the B.I.P.'s in Table 1 (in boldface type) refers to Solution 2; the figures placed in parentheses in italics between the B.I.P. data are the computed numerical differences between each two adjacent B.I.P. values.

Table 1 clearly shows that the sequence of the relative electromotive efficacies of the various ions is identical with the well-known sequence commonly referred to as the Hofmeister anion series, which has been observed in numerous widely different effects when specific ion-solvent interactions do not occur. Noteworthy is the magnitude of the B.I.P.'s observed, up to more than 400 mV in our cells with inorganic anions only.

The additivity rule states that the B.I.P. for any pair of critical ions should be the algebraic sum of the B.I.P.'s of any sequence of cells in which each sequential pair has one common critical ion as indicated above in Eq. (1). Thus, for the most extreme example, involving all seven species of critical ions in Table 1, we may write:

$$\begin{aligned}\mathrm{B.I.P.}_{\mathrm{ClO_4^-/IO_3^-}} &= \mathrm{B.I.P.}_{\mathrm{ClO_4^-/SCN^-}} + \mathrm{B.I.P.}_{\mathrm{SCN^-/I^-}} + \mathrm{B.I.P.}_{\mathrm{I^-/NO_3^-}} \\ &\quad + \mathrm{B.I.P.}_{\mathrm{NO_3^-/Br^-}} + \mathrm{B.I.P.}_{\mathrm{Br^-/Cl^-}} + \mathrm{B.I.P.}_{\mathrm{Cl^-/IO_3^-}}.\end{aligned} \tag{2}$$

The experimental $\mathrm{B.I.P.}_{\mathrm{ClO_4^-/IO_3^-}}$ is -442.8 mV; it is very close to the computed sum of the B.I.P.'s of the six sequential pairs of critical ions: $(-80.8\ \mathrm{mV}) + (-31.4\ \mathrm{mV}) + (-83.1\ \mathrm{mV}) + (-54.5\ \mathrm{mV}) + (-92.0\ \mathrm{mV}) + (-102.4\ \mathrm{mV})$, which equals -444.2 mV.

The consistency of the data of Table 1 becomes evident if one follows the dotted and broken lines which connect the measured B.I.P.'s of a given pair of anions (boldface figures) and the difference (italicized figures in parentheses) between the B.I.P.'s arising in cells containing one of those anions and a common third anion.

Many important studies concerning B.I.P. cells are still missing, they include: the investigation of cells with cation selective membranes; a comparative study of the influence of the chemical nature of anionic and cationic ion exchanger compounds on the magnitude of the B.I.P. and the sequence of ionic specificities; a similar investigation of the influence of the solvent of which the membranes mainly consist, including mixed solvents one of which may show some specific affinity for one or the other species

Table 1. Bi-ionic potentials in cells: 0.1 M aqueous electrolyte AL | liquid membrane | 0.1 M aqueous electrolyte AM[a]

Solution 1 (AL)	Solution 2 (AM)										
	KIO_3		KCl		KBr		KNO_3		KI		KSCN
$NaClO_4$[b]	**−442.8**	(*−101.0*)	**−341.8**	(*−92.7*)	**−249.1**	(*−53.6*)	**−195.5**	(*−83.0*)	**−112.5**	(*−31.7*)	**−80.8**
	(*−80.2*)		(*−81.2*)		(*−80.6*)		(*−81.1*)		(*−81.1*)		
KSCN	**−362.6**	(*−102.0*)	**−260.6**	(*−92.1*)	**−168.5**	(*−54.1*)	**−114.4**	(*−83.0*)	**−31.4**		
	(*−31.7*)		(*−31.1*)		(*−31.0*)		(*−31.3*)				
KI	**−330.9**	(*−101.4*)	**−229.5**	(*−92.0*)	**−137.5**	(*−54.4*)	**−83.1**				
	(*−83.4*)		(*−83.2*)		(*−83.0*)						
KNO_3	**−247.5**	(*−101.2*)	**−146.3**	(*−91.8*)	**−54.5**						
	(*−53.5*)		(*−54.3*)								
KBr	**−194.0**	(*−102.0*)	**−92.0**								
	(*−91.6*)										
KCl	**−102.4**										

[a] Temperature: 25 ± 0.05 °C; data in mV; the sign refers to Solution 2.

[b] $NaClO_4$ was used because $KClO_4$ is not soluble to the extent of 0.1 M.

of critical ions (a problem that blends gradually with the question of non-ionic ion carriers); the extension of B.I.P. studies to bivalent, polyvalent and organic critical ions; and the search for ion exchanger compounds whose various ionic forms show only minimal solubilities in water. Work on these topics is in progress.

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